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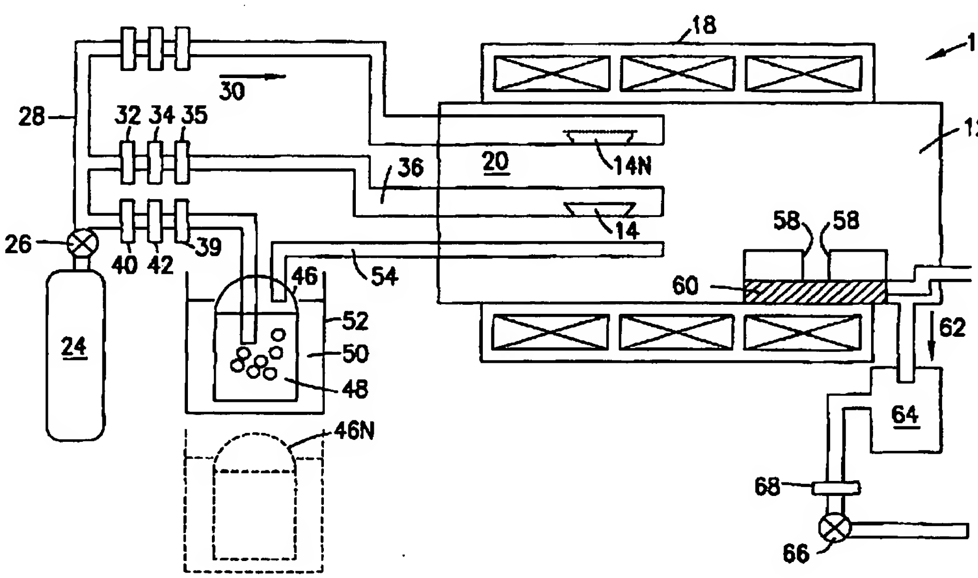

(57) Abstract

Methods for preparing organic thin films on substrates (58), the method comprising the steps of providing a plurality of organic precursors (14, 48) in the vapor phase, and reacting the plurality of organic precursors (14, 48) at a sub-atmospheric pressure. Also included are thin films made by such a method and apparatuses used to conduct such a method. The method is well-suited to the formation of organic light emitting devices and other display-related technologies.

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LOW PRESSURE VAPOR PHASE DEPOSITION OF ORGANIC THIN FILMS

GOVERNMENT RIGHTS

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FIELD OF THE INVENTION

The present invention relates to the fabrication of optical quality thin films, and more particularly to the low pressure fabrication of such thin films for application in non-linear optical devices and organic light emitting devices.

BACKGROUND OF THE INVENTION

The field of organic electroluminescence is a rapidly growing technology. Spurred by potential application to displays, organic light emitting devices (OLEDs) are capable of achieving external quantum efficiencies of over 3%, and operational lifetimes on the order of 10,000 hours at video brightness. Both small

molecule and polymer-based OLEDs are known, but polymer-based devices have a general advantage of simple and inexpensive fabrication by spin-on deposition techniques. In contrast, small molecule devices are usually fabricated by thermal evaporation in vacuum, which is usually a more expensive process than spin-on deposition. Examples of OLED structures and processing techniques are provided in published PCT application WO 96/19792, incorporated herein by reference.

The use of organic vapor phase deposition (OVPD) has made progress towards the low cost, large scale deposition of small molecular weight organic layers with numerous potential photonic device applications such as displays. The OVPD process is described in U.S. Patent No. 5,554,220 to Forrest et al.; S.R. Forrest et al., "Intense Second Harmonic Generation and Long-Range Structural Ordering in Thin Films of an Organic Salt Grown by Organic Vapor Phase Deposition," 68 Appl. Phys. Lett. 1326 (1996); and P.E. Burrows et al., "Organic Vapor Phase Deposition: a New Method for the Growth of Organic Thin Films with Large Optical Non-linearities," 156 J. of Crystal Growth 91 (1995), each of which is incorporated herein by reference.

The OVPD process uses carrier gases to transport source materials to a substrate, where the gases condense to form a desired thin film. The OVPD technique has been used, for example, to deposit films of the optically non-linear organic (NLO) salt, 4'-dimethylamino-N-methyl-4-stilbazolium tosylate (DAST), from volatile precursors 4'-

dimethylamino-N-methyl-4-stilbazolium iodide (DASI) and methyl p-toluensulfonate (methyltosylate, MT), which are transported by carrier gases to a heated substrate. In this process, DASI thermally decomposes to form 4-dimethylamino-4-stilbazole (DAS), which subsequently reacts with MT to form DAST on the substrate.

Because of its capability for controlled co-deposition of materials with radically different vapor pressures, OVPD is believed to be the only method for the precise stoichiometric growth of multi-component thin films. However, the OPVD process is conducted at atmospheric pressure, and films grown at or near atmospheric pressure are often rough and have non-uniform surface morphologies due to gas phase nucleation and a diffusion-limited growth process.

SUMMARY OF THE INVENTION

The present invention makes use of low pressure deposition techniques to produce organic thin films having superior surface properties. In one aspect, the present invention comprises a method for preparing an organic thin film on a substrate, the method comprising the steps of providing a plurality of organic precursors, the organic precursors being in the vapor phase; and reacting the plurality of organic precursors at a sub-atmospheric pressure in the presence of the substrate to form a thin film on the substrate. In another aspect, the present invention includes organic films made by such a method. In

yet another aspect, the present invention includes an apparatus designed to facilitate the reaction of organic precursors at sub-atmospheric pressures to form an organic film on a substrate.

One advantage of the present invention is that it provides multi-component organic thin films wherein the amount of each component in such films can be controlled accurately and precisely.

Another advantage of the present invention is that it provides uniform organic thin films having smooth surfaces.

Another advantage of the invention is that it provides a low pressure organic vapor phase deposition method and apparatus for the growth of thin films of organic light emitting materials and optically non-linear organic salts.

Another advantage of the invention is that it provides a low pressure organic molecular beam deposition method and apparatus for the formation of thin films of organic light emitting materials and optically non-linear organic salts.

Yet another advantage of the invention is that it provides a method and apparatus for the uniform deposition of organic materials over large substrate areas.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 shows a LPOVPD reactor, in accordance with an embodiment of the present invention.

Fig. 2 shows an OMVD reactor, in accordance with an embodiment of the present invention.

Fig. 3 shows an apparatus for the continuous low pressure deposition of organic materials onto substrates, in accordance with an embodiment of the present invention.

Figs. 4A and 4B are planar and cross-sectional views, respectively, of a reactant gas distributor, in accordance with an embodiment of the present invention.

Fig. 5 is a side view of a roll-to-roll substrate delivery mechanism, in accordance with an embodiment of the present invention.

DETAILED DESCRIPTION

The present invention provides a method and apparatus for the growth of organic thin films on substrates while under sub-atmospheric pressures. The method of the invention is herein identified as low pressure organic vapor deposition (LPOVPD). The LPOVPD method of the present invention allows for the accurate and precise control of the deposition of multi-component organic thin films. In addition, the thin films of the present invention are characterized by superior surface properties such as low surface roughnesses.

A LPOVPD reactor 10 in accordance with an embodiment of the present invention is schematically shown in Fig. 1. Reactor 10 includes a reaction chamber, such as a reactor tube 12, and tubing extending into the reaction chamber. Reactor tube 12 is a cylinder having a suitable

dimension such as, for example, a diameter of 10 cm and an approximate length of 45 cm in an experimental apparatus. Reactor tube 12 is made of any suitable material such as glass or quartz. An open container such as crucible 14 contains a first organic precursor material and is placed within tube 36 near one end 20 of the reactor tube 12. Alternatively, crucible 14 is placed directly on the reactor tube 12 or on shelves or tubes therein. Crucible 14 is heated or cooled by means of a multi-zone heater/cooler 18, which substantially surrounds reactor tube 12. The temperature control of crucible 14 results in the thermal decomposition or volatilization of the first organic precursor material within crucible 14. A regulated stream 30 of inert carrier gas is passed through tube 36 and into the reaction chamber, thus causing vapor of the first organic precursor to flow along the reactor tube 12 toward its exhaust end 22. The inert carrier gas is an inert gas such as nitrogen, helium, argon, krypton, xenon, neon and the like. Gases with a reducing character, such as hydrogen, ammonia and methane, are also inert for many organic materials. Use of these reducing gases often has the additional benefit of assisting in the burning of undesired excess reactants.

Inert gas is delivered from tank 24 through a regulator valve 26 and into tubing 28 for delivery through at least two flow paths, 30 and 38, and into reactor tube 12. One flow path 30 includes a series connected pressure regulator 32, flow meter 34 and quick switching valve 35

from which the carrier gas is delivered into end 20 of reactor tube 12. The second flow path 38 includes a series connected pressure regulator 40, flow meter 42 and quick switching valve 39 from which the carrier gas flows into a bubbler 46, which contains a second organic precursor material 48. To facilitate the temperature control of second organic precursor material 48, bubbler 46 is partially immersed in bath 50 within container 52. Inert gas from tank 24 bubbles through the second organic precursor 48 and through tubing 54 to carry vapor of the second organic precursor 48 into reactor tube 12. During this process, tube 54 must be maintained at a sufficiently high temperature to avoid recondensation of the volatilized second organic precursor 48 as it travels from the bubbler to the reactor.

The amount of any precursor entering reactor tube 12 is controlled by processing parameters such as the temperature and flow rate of the carrier gas and the temperature of the reactants. The LPOVPD method provides precise metering of the precursors or reactants independently of their vapor pressure or chemical nature using pressure mass flow controllers. The present method thus permits the combination of materials with widely different characteristics in ratios necessary for the production of desired films.

The precursor streams are capable of being turned on and off almost instantly by employing quick switching valves 35 and 39. These valves direct the precursor

streams into reactor 12 or into a by-pass line (not shown), so that at any given time, different precursor streams may be entering the reactor 12 for the deposition of films of different compositions and characteristics. Valve 39 also regulates the admittance of carrier gas into bubbler 46. Valves 35 and 39 thus allow the rapid change of reactant streams entering the reactor 12, for changing the nature and the composition of the grown films. It is thus possible, for example, to grow ABAB, ABCABC, ABABCAB, and ABCDABCD-type films, where each letter denotes a different molecular layer or composition.

A vacuum pump 66 and control throttle valve 68 are attached to reactor 10 at the exhaust 62. Most of the organic vapors not deposited onto substrate 58 are condensed in a trap 64 placed upstream from pump 66. Trap 64 contains liquid nitrogen or a neutral, fluorocarbon oil, for example. Throttle valve 68 regulates the pressure in reactor 10. An appropriate pressure gauge is connected to the reactor (not shown) with electronic feedback to the control throttle valve 68 to maintain a desired pressure in the reactor.

Vacuum pump 66 provides a pressure of about 0.001 - 100 Torr in reactor tube 12. The actual pressure for any combination of acceptor, donor, and single component layers is experimentally determined with reference to the temperatures required to volatilize the precursor materials, the wall temperature to prevent condensation of the precursor materials, and the reaction zone temperature

gradient. The optimal choice of pressure is unique to the requirements of each deposited organic layer. For example, optimal pressures for the deposition of single component layers such as tris-(8-hydroxyquinoline) aluminum (Alq_3) or N-N'-diphenyl-N,N-bis(3-methylphenyl) 1,1'-biphenyl-4,4'diamine (TPD) are about 0.1-10 Torr.

The substrates on which the thin films of the present invention are deposited are typically selected from those materials that are commonly encountered in semiconductor and optics manufacturing. Such materials include, for example, glass, quartz, silicon, gallium arsenide and other III-V semiconductors, aluminum, gold and other precious and non-precious metals, polymer films, silicon dioxide and silicon nitride, indium-tin-oxide and the like. For high quality optical thin films, it is preferable to use substrates that provide crystalline interactions with the deposited organic film to induce epitaxial growth. To achieve such epitaxial growth, it is often necessary to coat substrates with non-polar organics having crystalline structures similar to the film to be deposited.

In addition, as an organic thin film is deposited onto substrate 58, it is often desirable to control the temperature of the substrate. Independent control of substrate temperature is accomplished, for example, by contacting substrate 58 with temperature-control block 60, which has channels therein for the circulation of materials such as water, gas, freon glycerin, liquid nitrogen, and

the like. It can also be heated by the use of resistance or radiant heaters positioned on or near the block 60.

Reactor 20 of Fig. 1 is expandable to include multiple bubblers 46N to feed additional precursors into reactor 20. Similarly, multiple carrier gas flow paths 30N are used to deliver yet additional precursors from crucibles 14N. As an alternative, crucibles 14, 14N are vertically stackable on shelves or in tubes within reactor tube 12 for processing the additional precursors. Depending on the organic film to be deposited, one or more flow paths 30, 38 are used alone or in any combination to provide the necessary precursor materials.

The method of the present invention is used to deposit a wide variety of organic thin films from the reaction of vapor precursors. As used herein, "reaction" refers to a chemical reaction in which precursor reactants form a distinct reaction product, or alternatively, it merely refers to a combination or mixture of precursor materials, or where precursor materials form a donor-acceptor or quest-host relationship. For example, in accordance with the present invention, the following NLO materials are formed as thin films by the reaction of the listed precursors:

Film Material	First Precursor	Second Precursor
4'-dimethylamino-N-methyl-4-stilbazolium tosylate (DAST)	4'-dimethylamino-4-stilbazole (DAS)	methyl tosylate (MT)
4'-dimethylamino-4-methylstilbazolium methanesulfonate (DASM)	methyl methanesulfonate (MM)	4'-dimethylamino-4-stilbazole (DAS)
4'-dimethylamino-4-methylstilbazolium trifluoromethanesulfonate (DASM$_f$)	methyl trifluoromethanesulfonate (M$_f$M)	4'-dimethylamino-4-stilbazole (DAS)
4'-dimethylamino-N-methyl-4-stilbazolium tosylate (DAST)	methyl tosylate (MT)	4'-dimethylamino-4-methylstilbazolium thiophenoxide (DASTh)
4'-methoxy-4-methylstilbazolium tosylate (MeOST)	methyl tosylate (MT)	4'-methoxy-4-methylstilbazole (MeOS)
4'-dimethylamino-N-methyl-4-stilbazolium tosylate (DAST)	methyl tosylate (MT)	4'-dimethylamino-4-ethylstilbazolium iodide (DAS(Et)I)
4'-dimethylamino-N-methyl-4-stilbazolium tosylate (DAST)	methyl tosylate (MT)	4'-dimethylamino-4-ethylstilbazolium hydroxide (DAS(Et)OH)
4'-dimethylamino-4-acetylstilbazolium tosylate (DAAST)	acetyl toluenesulfonate (AT)	4'-dimethylamino-4-stilbazole (DAS)
4'dimethylamino-4-methylstilbazolium trifluoroacetate (DASA$_f$)	methyl trifluoroacetate (MA$_f$)	4'-dimethylamino-4-stilbazole (DAS)

In another example relating more specifically to light emitting materials used to make OLEDs, the precursors consist of, for example, tetrathisferlvalene (TFF) and 7,7,8,8-tetracyanoquinodimethane (TCNQ). The mixing step results in the charge transfer complex TTF-TCNQ which deposits onto a substrate. In another example relating to OLEDs, 4-(dicyanomethylene)-2-methyl-6-(p-dimethylaminostyryl)-4H-pyran (DCM) is added into a high flow rate carrier gas stream while Alq_3 is added into a lower flow rate carrier gas stream. These streams are then

mixed in a central reactor tube, thus providing the desired dilution of the guest molecule in the host matrix film to form a single luminescent layer. Other guest molecule examples in Alq_3 hosts are 5,10,15,20-tetraphenyl-21H,23H-porphine (TPP), Rubrene, DCM2, Coumarin, etc. As a variation, multiple dopants can be added into a single host to achieve efficient broad color conversion.

In another example, a bilayer light emitting device consisting of a hole transporting layer ("HTL") such as TPD; α-4,4'-bis[N-(1-naphthyl)-N-Phenyl-amino] biphenyl (α-NPD); or MTDATA, layered onto the surface of a light emitting layer ("EL") such as Alq_3, bis-(8-hydroxyquinoline) aluminum oxyphenyl ($(Alq_2)'$-OPh) or doped combinations of these layers, is grown by sequentially growing the HTL and EL to desired thicknesses. This is followed by growing additional layers onto the organics, or by growth on metallic contact layers using organometallic sources such as trimethyl-indium, trimethyl-gallium, and the like.

In addition to the apparatus and method described with reference to Fig. 1, the present invention includes a low pressure reactor 70 and method as shown in Fig. 2. Reactor 70 includes a modified ultra-high vacuum chamber 71 and a vacuum pump such as a turbomolecular pump (not shown) connected to valve 72. Typical chamber base pressures in chamber 71 are 10^{-8} - 10^{-11} Torr. The process of depositing organic layers with the use of reactor 70 is called organic molecular beam vapor deposition (OMVD). Although both

LPOVPD and OMVD make use of sub-atmospheric pressures for the deposition of organic layers, the principle difference between these processes is that in the latter, the molecular mean free path is comparable to or larger than the dimensions of the chamber 70. In comparison, the mean free path in LPOVPD is significantly shorter than the gas reactor dimensions. OMVD thus allows for the formation of highly directed molecular "beams" from the injectors to the substrate, allowing for precise kinetic control of the grown film thickness, purity and morphology.

Bubbler 74 is included for containing a first precursor material 75. The bubbler 74 is placed into container 76 and immersed in a temperature controlled bath 80. A high purity inert carrier gas 78 bubbles through first precursor 75, and carries respective vapors through heated tubing 79 and into vacuum chamber 71 by way of injector 82. Once inside chamber 71, the precursor vapors form a molecular beam 83 that impinges on substrate 85. Substrate 85 is provided with a means for providing temperature control such as coolant port 81, for example.

Vacuum chamber 71 optionally is provided with at least one Knudsen or K-cell 86, which contains a second precursor material 88. K-cell 86 is a uniformly heated and controlled oven for the effusion of evaporants under vacuum. For example, K-cell 86 is heated to crack DASI or other precursor and sublime the resulting DAS, such that it is injected into reactor 70 as a molecular beam 89. Alternatively, K-cell 86 simply sublimes a single component

substance such as Alq_3. Alternatively, K-cell 86 is fitted with a carrier gas inlet used to dilute the concentration of the molecular species being sublimed or evaporated into the gas stream by thermalization. This dilution process is particularly useful in achieving precise doping levels of guest-host systems such as DCM-Alq_3 by controlling the temperatures of bath 80 and Knudsen cell 86 as well as the flow of carrier gas 78 to bubbler 74.

Molecular beams 83 and 89 impinge on substrate 85 to deposit an organic thin film, the thickness of which is monitored by quartz crystal 93. Sample holder 90 rotates to ensure a uniform deposition and reaction of precursor materials. The deposition of precursor materials is further controlled by shutters 87, which are used to interrupt molecular beams 83 and 89.

Reactor 70 also optionally includes a cooled shroud 91 to help keep the pressure of vacuum chamber 71 to a minimum for re-evaporated precursor materials. Also preferably included is a partition 92 to keep precursor materials from migrating and thus contaminating each other.

Reactor 70 is embellished with many of the same attributes of the LPOVPD reactor shown in Fig. 1, such as quick switching valves, bypass lines and the like. Reactor 70 is able to be fitted with multiple Knudsen cells and bubblers for the deposition of multiple precursor materials onto substrate 85. Reactor 70 also preferably includes a "load-lock" 94 for sample introduction. Load-lock 94 includes door 95 and vacuum pump 96, and provides for the

exchange of samples without compromising the pressure of chamber 71.

The apparatus of Fig. 1 is optionally modified for the continuous deposition of organic layers on large area substrates, as shown by the example illustrated in Fig. 3. The apparatus of Fig. 3 includes a plurality of vacuum chambers such as loading chamber 146, organic layer deposition chambers 150 and 152, contact deposition chamber 154, and unload chamber 156. As an example, each deposition chamber is a LPOVPD reactor 10 of Fig. 1. The substrates 137 are transported on a conveyor belt 148 through each of chambers 150, 152, 154 and 156. In the embodiment shown in Fig. 3, chambers 150, 152 and 154 include sources 158, 160 and 162, respectively, of radiant heat to prevent the condensation of organic vapors. Although only two organic layer deposition chambers 150 and 152 are shown in Fig. 3, additional chambers are included as desired. In passing from the loading chamber 146 to the organic layer deposition chambers 150 and 152, and from the contact deposition chamber 154 to the unload chamber 156, the substrate 137 passes through air locks (not shown) so as not to compromise the vacuum in the chambers 150, 152, and 154. As an example relating to OLEDs, chambers 150 and 152 are used for the deposition of TPD and Alq_3, respectively, and chamber 154 is used for the deposition of an Mg:Ag contact layer.

Each of the chambers 150, 152, and 154 in the example of Fig. 3 includes a reactant gas distributor (RGD)

108 for the deposition of organic precursor materials, as shown in detail in Figs. 4A and 4B. RGD's 108 are used as an alternative to the organic precursor delivery mechanisms of Figs. 1 and 2, and are used to provide gas curtains, 120, 120 ', 120 '' and 120 '''. RGD 108 ensures that where multiple organic precursors are deposited, the precursors remain separated until deposited on a substrate, whereupon reaction of the precursors is permitted to take place. RGD 108 includes heater 122, second carrier gas inlet 112 and gas manifold 132. Heater 122 prevents the premature condensation of organic precursor materials. Over RGD 108 is a first carrier gas inlet 114 and distributor plate 110. First carrier gas inlet 114 supplies gas which usually carries a first organic precursor of generally low volatility such as, for example, MT. The first carrier gas enters a reaction chamber though distributor plate 110, which is a wire mesh, a glass filter material, or a porous stainless steel plate, for example. The column of carrier gas flowing through distributor plate 110 is shadowed by the RGD 108. RGD 108 provides a planar gas curtain 120 of a second organic precursor of generally low vapor pressure such as, for example, DAS. A second carrier gas containing a second organic precursor enters at inlet 112 and is directed into gas manifold 132. Manifold 132 is a hollow tube having a line of holes 134 for feeding the second carrier has into an annular cavity 126, which surrounds manifold 132. Second carrier gas exits RGD 108 through slit 136, thus giving it the shape of a planar curtain.

As an example, curtain 120 is comprised of TPD vapors, curtain 120' is comprised of Alq_3 vapors and curtain 120'' is comprised of vapors such as a polypyrole or metallorganic compounds that produce a conductive surface. If desired, control or tuning of the color of light emitted by an OLED can be effected by suitable doping of the Alq_3 layer with an additional RGD device 108 in the chamber 152 that produces a curtain 120''' of dopant vapor.

The apparatus of Fig. 1, Fig. 2 or Fig. 3 is optionally modified by using a "roll-to-roll" substrate delivery system, as shown in Fig. 5. The delivery system shown in Fig. 5 is suitable for the deposition of organic thin films onto large area, flexible substrates. Substrate 180 is made of a polymer sheet or metal foil, for example, and is delivered from roll 181 to roll 182. The deposition of organic precursors onto substrate 180 occurs when substrate 180 is unrolled from roll 181 and is therefore exposed to the reaction chamber of Fig. 1, or when exposed to the molecular beam or curtains of Figs. 2 and 3, respectively. Rolls 181 and 182 are driven by any suitable means, such as a variable speed motor. The speed at which substrate 180 is passed from roll 181 to roll 182 dictates the thickness of the organic film that forms on substrate 180.

The present invention is further described with reference to the following non-limiting examples.

Example 1

Using the apparatus of Fig. 1, layers of organic light emitting materials were grown using glass and flexible polyester substrates precoated with transparent layers of indium tin oxide (ITO). The ITO forms the anode of the device with a thickness of 1700Å and 1200Å for the glass and polyester substrates, respectively, yielding anode resistances of 10 Ω and 60 Ω, respectively. Glass substrates were cleaned by rinsing in a solution of detergent and deionized water in an ultrasonic bath, and then boiling in 1,1,1-trichloroethane, rinsing in acetone and finally rinsing in 2-propanol. To avoid damage due to exposure to organic solvents, the flexible substrates were cleaned by rinsing only in the detergent and 2-propanol solutions.

Glass substrates were placed within the reactor tube 12 at a location where the temperature was approximately 220°C. The first layer deposited on the ITO surface was TPD, a hole transporting material. Specifically, TPD vapor was carried from crucible 14 to substrate 28 via nitrogen carrier gas. The TPD growth conditions included a source temperature of 200± 5°C, a nitrogen carrier gas flow rate of 100 sccm, a reactor pressure of 0.50 Torr and a growth time of 20 minutes. At a nitrogen flow rate of 100 sccm, the Reynolds number of the system was ~500, indicating operation well within the laminar flow regime. The TPD layer was grown to a thickness of between 100 - 300Å.

After deposition, the temperature near the TPD crucible was reduced, and the corresponding nitrogen flow was shut off. Next, an electron transporting layer of Alq_3 was grown by turning on a separate nitrogen line to carry Alq_3 vapor from crucible 14N into chamber 12. The Alq_3 growth conditions included a source temperature of 247 ± 8°C, a nitrogen flow rate of 50 sccm, a pressure of 0.65 Torr and a growth time of 10 minutes. During the deposition of both the TDP and Alq_3, the substrate was maintained at 15°C using a water cooled stainless steel substrate holder. The TPD layer was grown to a thickness of between 700 - 1100Å.

After deposition of the Alq_3 layer, the substrate was removed from the reactor and a Mg:Ag top contact was applied by thermal evaporation. The contact was completed with the evaporation of a 1000Å thick protective Ag layer.

The use of low pressures during deposition resulted in organic layers having smooth and uniform surfaces. For example, the TPD and Alq_3 layers were measured via atomic force microscopy to have RMS roughnesses of 6-8Å and 9-11Å, respectively. The resulting OLED devices exhibited current-voltage characteristics wherein $I \alpha V$ at low voltages and $I \alpha V^9$ at higher voltages. The turn-on voltage, V_T, at which the power law dependence of I on V changed, was about 6V.

Example 2

An NLO film was prepared using the apparatus shown in Fig. 1. MT 48 was loaded into a 30 cm^3 bubbler 46, the temperature of which was maintained at approximately 80°-100°C by silicone oil bath 50. Nitrogen gas was used to bubble through the MT 48, thereby carrying MT vapor through glass tube 54 and into reactor tube 12 at a location approximately 5 cm beyond crucible 14, which contained was placed on the floor of reactor tube 12 and DASI. The pressure within reactor tube 12 was maintained at about 10^{-2} torr. DAS vapor reacted with the MT vapor to form a solid film of DAST on substrates 58, which were supported on substrate block 60. Excess unreacted MT vapor and any volatile side-reaction products were exhausted from exhaust tube 62. DAST films thus formed are useful as optical switches, for example.

The present invention makes use of low pressure deposition techniques to produce organic thin films having superior surface properties and accurate and precise compositions. Although various embodiments of the invention are shown and described herein, they are not meant to be limiting. For example, those of skill in the art may recognize certain modifications to these embodiments, which modifications are meant to be covered by the spirit and scope of the appended claims.

The subject invention as disclosed herein may be used in conjunction with co-pending applications: "High Reliability, High Efficiency, Integratable Organic Light Emitting Devices and Methods of Producing Same", Serial No. 08/774,119 (filed December 23, 1996); "Novel Materials for Multicolor LED's", Serial No. 08/850,264 (filed May 2, 1997); "Electron Transporting and Light Emitting Layers Based on Organic Free Radicals", Serial No. 08/774,120 (filed December 23, 1996); "Multicolor Display Devices", Serial No. 08/772,333 (filed December 23, 1996); "Red-Emitting Organic Light Emitting Devices (LED's)", Serial No. 08/774,087 (filed December 23, 1996); "Driving Circuit For Stacked Organic Light Emitting Devices", Serial No. 08/792,050 (filed February 3, 1997); "High Efficiency Organic Light Emitting Device Structures", Serial No. 08/772,332 (filed December 23, 1996); "Vacuum Deposited, Non-Polymeric Flexible Organic Light Emitting Devices", Serial No. 08/789,319 (filed January 23, 1997); "Displays Having Mesa Pixel Configuration", Serial No. 08/794,595 (filed February 3, 1997); "Stacked Organic Light Emitting Devices", Serial No. 08/792,046 (filed February 3, 1997); "High Contrast Transparent Organic Light Emitting Device Display", Serial No. 08/821,380 (filed March 20, 1997); "Organic Light Emitting Devices Containing A Metal Complex of 5-Hydroxy-Quinoxaline as A Host Material", Serial No. 08/838,099 (filed April 15, 1997); "Light Emitting Devices Having High Brightness", Serial No. 08/844,353 (filed April 18, 1997); "Organic Semiconductor Laser", Serial No.

60/046,061 (filed May 9, 1997); "Organic Semiconductor Laser", Serial No. 08/859,468 (filed May 19, 1997); "Saturated Full Color Stacked Organic Light Emitting Devices", Serial No. 08/858,994 (filed May 20, 1997); "An Organic Light Emitting Device Containing a Hole Injection Enhancement Layer", Serial No. 08/865,491 (filed May 29, 1997); "Plasma Treatment of Conductive Layers", Serial No. PCT/US97/10252; (filed June 12, 1997; Patterning of Thin Films for the Fabrication of Organic Multi-Color Displays", Serial No. PCT/US97/10289 (filed June 12, 1997); "Double Heterostructure Infrared and Vertical Cavity Surface Emitting Organic Lasers", Serial No. 60/053,176 (filed July 18, 1997); "Oleds Containing Thermally Stable Asymmetric Charge Carrier Materials", Serial No. 08/929,029 filed (September 8, 1997), "Light Emitting Device with Stack of Oleds and Phosphor Downconverter", Serial No. 08/925,403 (filed September 9, 1997), "An Improved Method for Depositing Indium Tin Oxide Layers in Organic Light Emitting Devices", Serial No. 08/928,800 (filed September 12, 1997), "Azlactone-Related Dopants in the Emissive Layer of an Oled" (filed October 9, 1997), Serial No. 08/948,130, "A Highly Transparent Organic Light Emitting Device Employing A Non-Metallic Cathode", (filed November 3, 1997), Attorney Docket No. 10020/40 (Provisional), and "A Highly Transparent Organic Light Emitting Device Employing a Non-Metallic Cathode", (filed November 5, 1997), Attorney Docket No. 10020/44, each co-pending application being incorporated herein by reference in its entirety. The

subject invention may also be used in conjunction with the subject matter of each of co-pending U.S. patent application Serial Nos. 08/354,674, 08/613,207, 08/632,322 and 08/693,359 and provisional patent application Serial Nos. 60/010,013, 60/024,001 and 60/025,501, each of which is also incorporated herein by reference in its entirety.

What is claimed is:

1. A method for preparing an organic thin film on a substrate, said method comprising the steps of:

providing a plurality of organic precursors, said organic precursors being in the vapor phase; and

reacting said plurality of organic precursors at a sub-atmospheric pressure in the presence of said substrate to form said thin film on said substrate.

2. The method of claim 1, wherein said substrate is located in a reaction chamber.

3. The method of claim 2, further comprising the step of transporting one of said plurality of organic precursors into said reaction chamber prior to said step of reacting.

4. The method of claim 3, wherein said step of transporting includes the step of using an inert gas to carry said transported organic precursor into said reaction chamber.

5. The method of claim 4, wherein said inert gas is selected from the group consisting of nitrogen, argon, helium, neon, krypton and xenon.

6. The method of claim 1, wherein at least one of said plurality of organic precursors is selected from the group consisting of MT, DASI, MM, M_fM, DASTh, MeOSI, DAS(Et)I, DAS(Et)OH, acetyl toluenesulfonate, MA_f, TTF, TCNQ, DCM, Alq_3, TPP, TPD, α-NPD, MTDATA, and $(Alq_2)'$-OPh.

7. The method of claim 3, further comprising the step of volatilizing said transported organic precursor prior to said step of transporting.

8. The method of claim 7, wherein:

said step of volatilizing includes the step of loading said transported organic precursor into a bubbler; and

said step of transporting includes the step of passing an inert gas through said bubbler for carrying said transported organic precursor into said reaction chamber.

9. The method of claim 7, wherein:

said step of volatilizing includes the steps of placing said transported organic precursor into an open container and heating said open container; and

said step of transporting includes the step of passing an inert gas over said open container

for carrying said transported organic precursor into said reaction chamber.

10. The method of claim 7, wherein said step of volatilizing includes the steps of:

loading said transported organic precursor into a Knudsen cell, said Knudsen cell extending into said reaction chamber; and

heating said Knudsen cell.

11. The method of claim 1, wherein the substrate is mounted to a rotating sample holder.

12. The method of claim 1, wherein said sub-atmospheric pressure is within the range of about 10^{-11} - 10^{2} torr.

13. An organic film produced by the method of claim 1.

14. The organic film of claim 13, wherein said film comprises a light emitting material.

15. The organic film of claim 13, wherein said film comprises an optically non-linear material.

16. An apparatus for preparing an organic thin film on a substrate, said apparatus comprising:

a reaction chamber;

a heater substantially surrounding said reaction chamber;

tubing extending into said reaction chamber; and

a vacuum pump attached to said reaction chamber.

17. The apparatus of claim 16, wherein said reaction chamber comprises a reactor tube.

18. The apparatus of claim 16, wherein said heater is a multi-zone heater/cooler.

19. The apparatus of claim 16, wherein said tubing comprises:

a tube having a first end and a second end, the second end of said tube extending into said reaction chamber; and

a gas source connected to the first end of said tube.

20. The apparatus of claim 19, further comprising an open container located inside of said tube, said open container for holding organic precursor material.

21. The apparatus of claim 20, wherein said tube includes a pressure regulator and a valve.

22. The apparatus of claim 16, wherein said tubing comprises:

a first tube having a first end and a second end, said second end of said first tube extending into said reaction chamber;

a bubbler connected to the first end of said first tube, said bubbler for containing organic precursor material;

a second tube having a first end and a second end, said second end of said second tube connected to said bubbler; and

a gas source connected to the first end of said second tube.

23. The apparatus of claim 22, wherein said second tube includes a pressure regulator and a valve.

24. The apparatus of claim 16, further comprising a temperature-control block in contact with the substrate, said temperature-control block having a channel therein.

25. The apparatus of claim 16, further comprising a trap attached to said reaction chamber.

26. The apparatus of claim 16, further comprising a first roll and a second roll in said reaction chamber for

passing the substrate between said first and second rolls.

27. An apparatus for preparing an organic thin film on a substrate, said apparatus comprising:

a reaction chamber;

a Knudsen cell extending into said reaction chamber;

a sample holder connected to the substrate; said sample holder being rotatable; and

a vacuum pump attached to said reaction chamber.

28. The apparatus of claim 27, further comprising tubing extending into said reaction chamber, said tubing comprising:

a first tube having a first end and a second end, said second end of said first tube extending into said reaction chamber;

a bubbler connected to the first end of said first tube, said bubbler for containing organic precursor material;

a second tube having a first end and a second end, said second end of said second tube connected to said bubbler; and

a gas source connected to the first end of said second tube.

29. The apparatus of claim 27, wherein said first tube is heated.

30. The apparatus of claim 27, further comprising a cooled shroud in said reaction chamber.

31. The apparatus of claim 27, further comprising a sensor for detecting the thickness of the thin firm.

32. The apparatus of claim 31, wherein said sensor is a quartz crystal.

33. The apparatus of claim 27, further comprising a load-lock connected to said reaction chamber.

34. The apparatus of claim 27, wherein said vacuum pump is a turbomolecular pump.

35. The apparatus of claim 27, further comprising a first roll and a second roll in said reaction chamber for passing the substrate between said first and second rolls.

36. An apparatus for preparing an organic thin film on a substrate, said apparatus comprising:

a plurality of vacuum chambers, said plurality of vacuum chambers including a loading

chamber and an organic layer deposition chamber; and

a conveyor belt passing through said plurality of vacuum chambers, said conveyor belt having a substrate thereon.

37. The apparatus of claim 36, wherein said organic layer deposition chamber includes a reactant gas distributor.

38. The apparatus of claim 36, wherein said organic layer deposition chamber includes a heater.

39. The apparatus of claim 36, further comprising a contact deposition chamber.

40. An apparatus for preparing an organic thin film on a substrate, said apparatus comprising:

a reaction chamber;

means for heating said reaction chamber;

means for introducing vapors of organic precursor materials into said reaction chamber; and

means for reducing the pressure in said reaction chamber to below atmospheric pressure.

41. A method for preparing an OLED, said method comprising the steps of:

providing a plurality of organic precursors, said organic precursors being in the vapor phase; and

reacting said plurality of organic precursors at a sub-atmospheric pressure.

42. The method of claim 41, wherein said organic precursors are light emitting materials.

43. The method of claim 41, wherein said step of reacting results in the formation of a light emitting material.

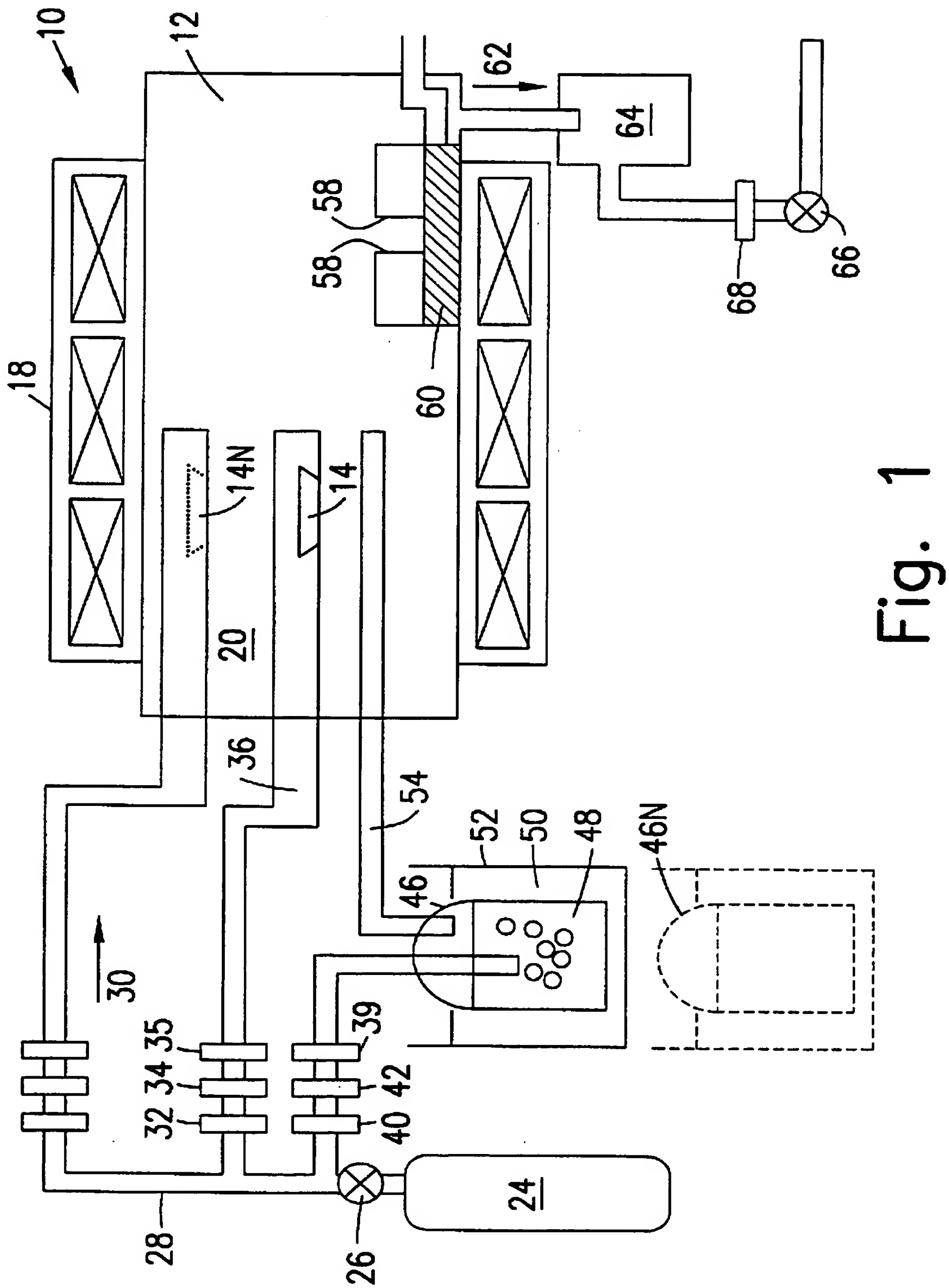
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Fig. 1

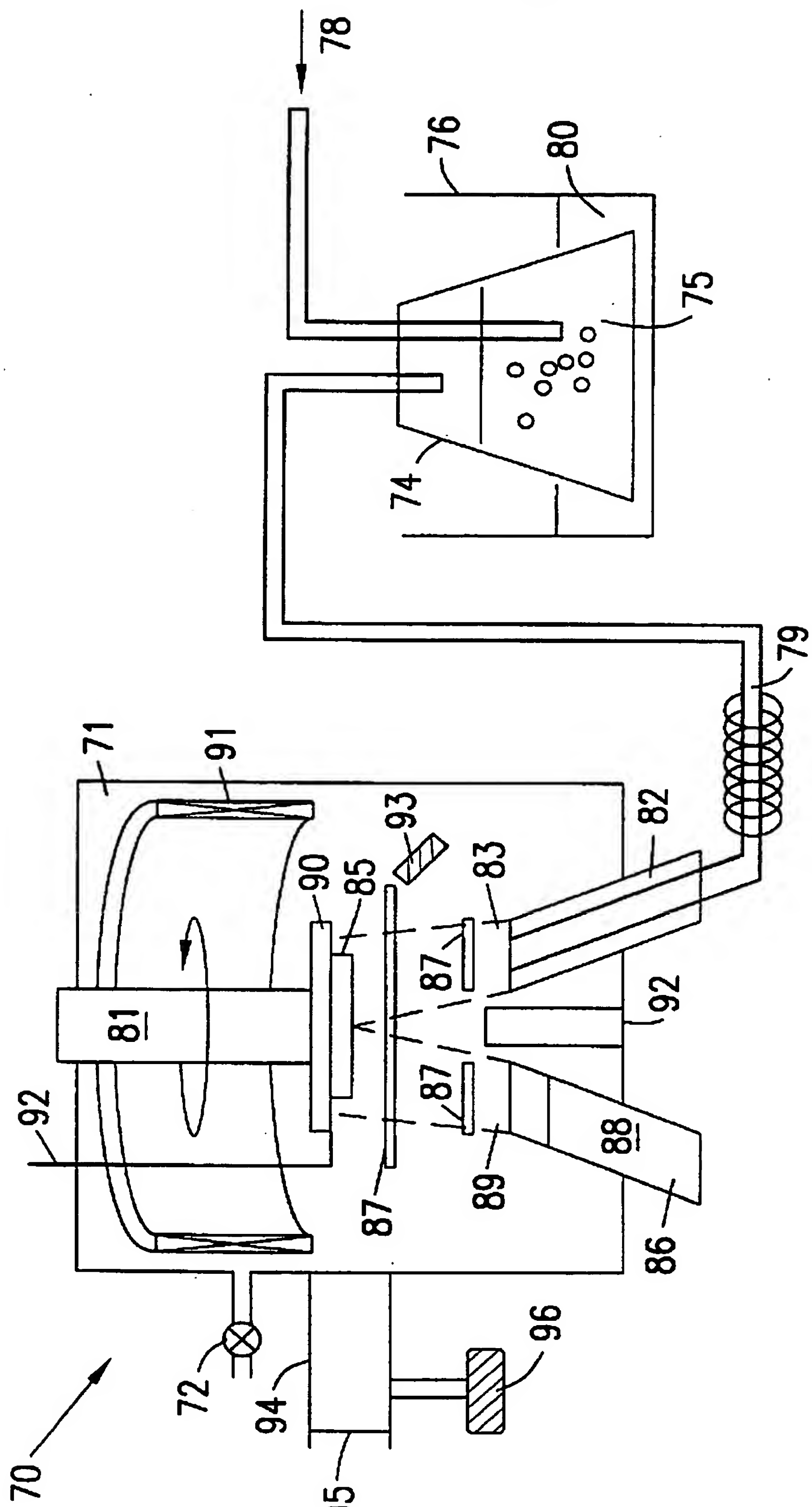
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Fig. 2

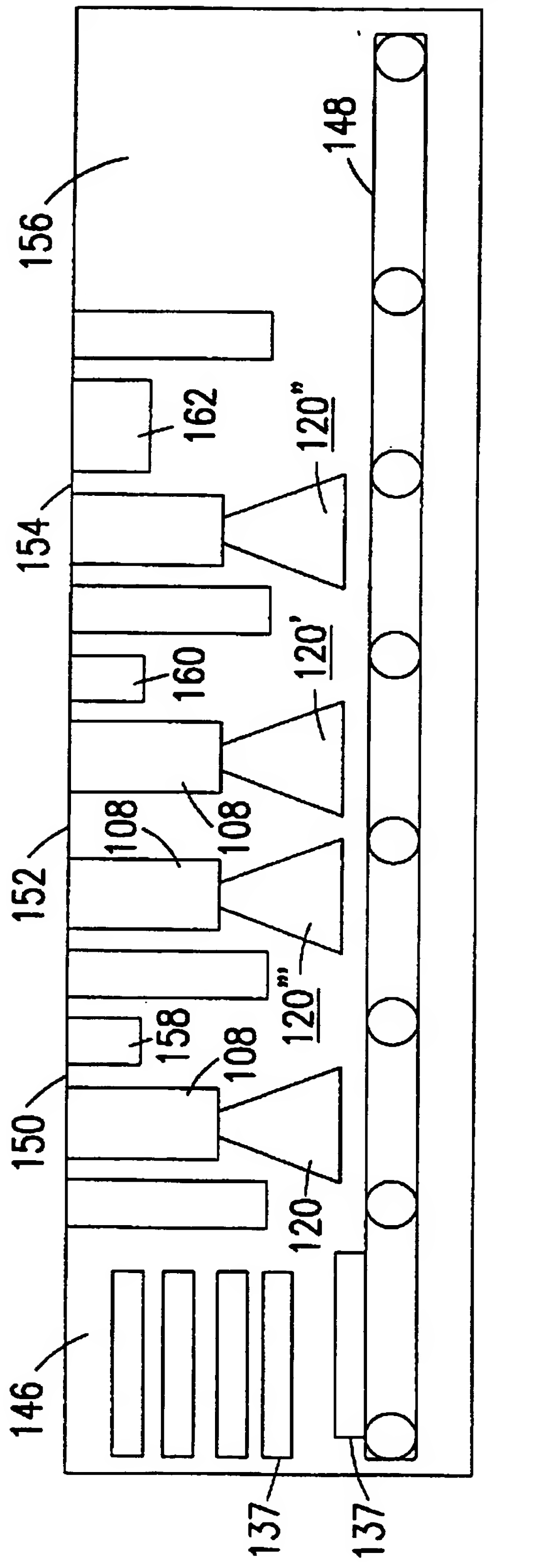
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Fig. 3

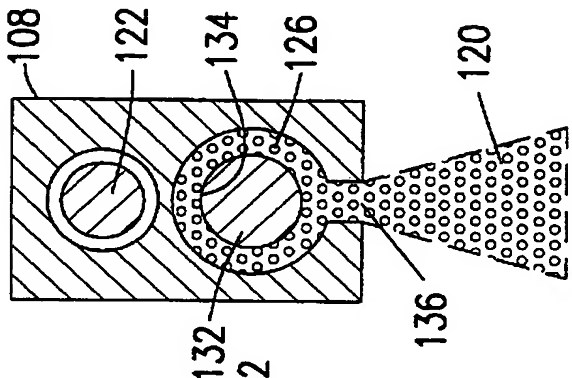

Fig. 4B

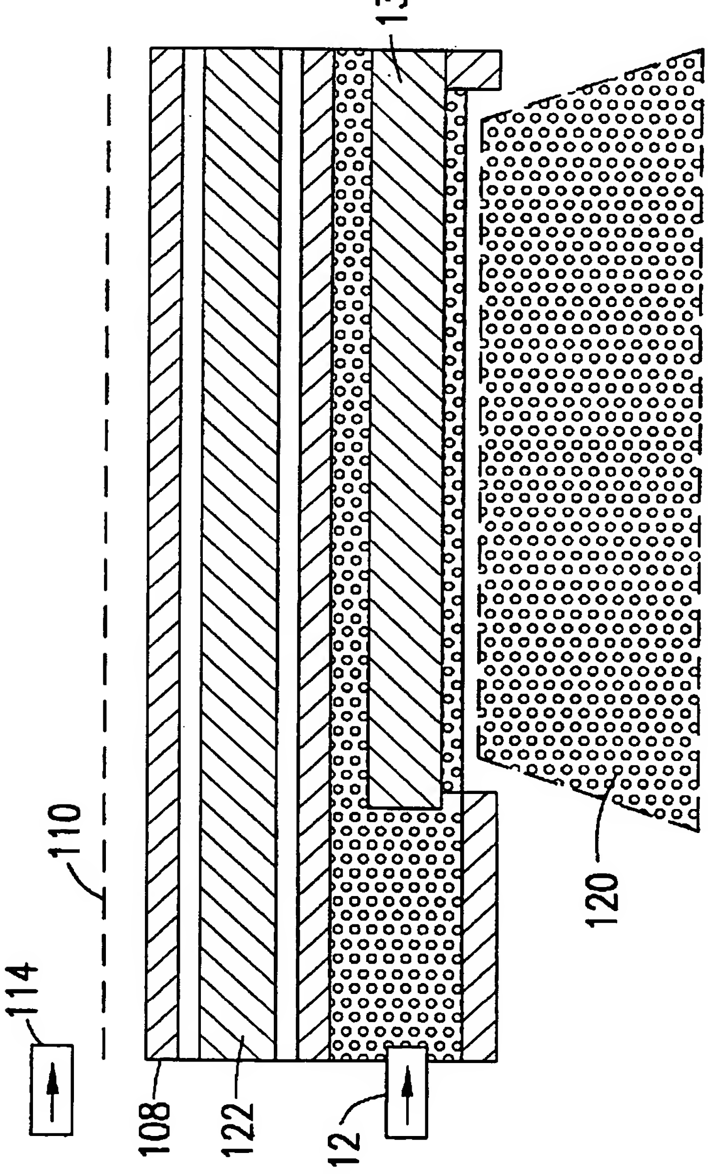

Fig. 4A

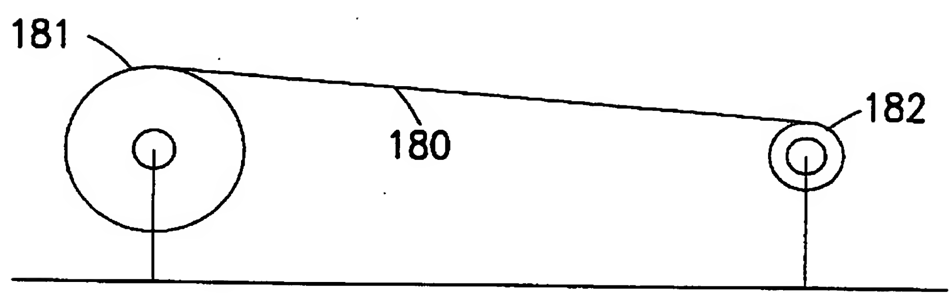

Fig. 5

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/24424

A. CLASSIFICATION OF SUBJECT MATTER
IPC(6) : C23C 16/00; H01J 1/62
US CL :Please See Extra Sheet.
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 427/64, 66, 255.1, 255.5, 255.6; 117/925, 927; 118/718, 719, 726; 313/503, 504, 506, 511

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS, STN

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X -- Y	US 5,670,212 A (STARING et al.) 23 September 1997, Figure 1, col. 3, lines 30-55, col. 4, lines 1-40, example 1.	1-5, 7, 9, 12-14, 40-43 --- 11
X - Y	JP 06-279991 A (MITSUBISHI ELECTRIC CORP) 04 October 1994, abstract, figure 1, cols. 11 and 12.	1-3, 7, 10, 12, 13, 40 ---- 4-6, 8, 9, 11
X	JP 63-453362 A (MATSUSHITA ELECTRIC IND KK) 26 February 1988, abstract, figure 1, page 2.	1-3, 7, 12-14, 40-43

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

- * Special categories of cited documents:
- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed
- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
09 FEBRUARY 1999	01 MAR 1999

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/24424

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X - Y	US 5,554,220 A (FORREST et al.) 10 September 1996, figure 2, col. 4, line 62 to col. 5, line 10, col. 8, lines 40-45.	13-15 ---- 4-6, 8, 9, 11
X	US 4,681,773 A (BEAN) 21 July 1987, figure 1, col. 2, line 60 to col. 3, line 15, col. 4, lines 40-65, col. 5, lines 1-30.	27, 30, 33-40
X	US 5,039,657 A (GOLDMAN et al.) 13 August 1991, figure 1, cols. 6 and 7.	16-19, 22-25, 27-34, 40
X	US 5,334,250 A (MIKAMI et al.) 02 August 1994, figures 1 and 2, abstract.	16-21, 40
X	US 3,379,803 A (TITTMANN et al.) 23 April 1968, figures 1 and 2, col. 3, line 50 to col. 4, line 30.	16-19, 25, 26, 40
X	US 5,431,958 A (DESU et al.) 11 July 1995, figure 1,	16-19, 22-25

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/24424

A. CLASSIFICATION OF SUBJECT MATTER:
US CL :

427/64, 66, 255.1, 255.5, 255.6; 117/925, 927; 118/718, 719, 726; 313/503, 504, 506, 511